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An Introduction to Hydrogen Research in Alberta

Projects supported in part
by the Alberta/Canada
Energy Resources
Research Fund

1991
Edmonton

Alberta
ENERGY
Research and Technology Branch

ISBN 0-86499-827-9

Pub. No. I/415

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Foreword

Beginning in 1976, numerous projects were initiated in Alberta by industry and academic research institutions to help make better use of Alberta's energy resources.

These research, development and demonstration efforts were funded by the Alberta/Canada Energy Resources Research Fund (A/CERRF), which was established as a result of the 1974 agreement on oil prices between the federal government and the producing provinces.

Responsibility for applying and administering the fund rested with the A/CERRF Committee, made up of senior Alberta and federal government officials.

A/CERRF program priorities focused primarily on coal, energy conservation and renewable energy, and conventional energy resources. In 1988/89, a hydrogen research component was added.

Administration for the A/CERRF program was provided by staff within the Research and Technology Branch of Alberta Energy.

The A/CERRF program ended March 31, 1991. Although project funding has ceased, a series of technology transfer booklets, begun in 1986, continues to make research results available to industry and others who can use the information. This service will continue until all A/CERRF projects have been described.

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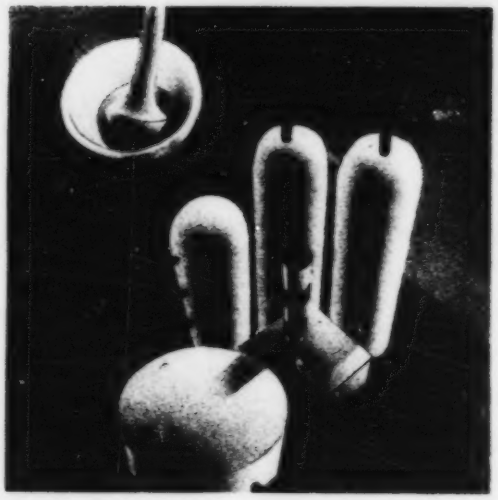


Long before atmospheric pollution and the "Greenhouse Effect" became topics of everyday conversation, a few scientists from around the world recognized that it was only a matter of time before mankind would have to move away from using fossil fuels, and toward other energy forms. They said this would become necessary partly because fossil fuel supplies would run out eventually or become uneconomic to use, and partly because the evolution of technology would make the impossible possible. These changes, therefore, would lead inevitably to the use of cleaner or alternative fuels. The clean fuel advocated by these scientists as having the best chance for success is hydrogen.

Mankind's use of fuels can be viewed as a series of waves passing through time: the first wave being wood, the second being coal, the third oil, and now natural gas. Each of these transitions involved using a fuel that contained increasing amounts of hydrogen relative to carbon (called the hydrogen-to-carbon ratio) and the ability to release greater amounts of energy. The ultimate transition will be to a fuel that contains no carbon whatsoever.

In the meantime, hydrogen is and will remain a valuable commodity in the fossil fuel and fertilizer industries upon which Alberta's economy strongly depends. Therefore, finding ways to produce and use hydrogen more efficiently will be of direct benefit to Alberta immediately. Someday, the technologies so developed may help bring about the technological changes that are necessary for the "Hydrogen Age" to reach its full potential.

Background

Hydrogen exists virtually everywhere on earth, but most people are not aware of this because hydrogen is usually found in combination with other elements. Enormous quantities of hydrogen are combined with oxygen in water, and appreciable amounts of it are found in a combined state in some minerals, hydrocarbons and all plants and animals.

Occasionally, molecular hydrogen, uncombined with other elements, can be found in volcanic gases and in trace amounts in the upper atmosphere, but these are not practical sources. Although hydrogen is too reactive for much of it to be found in a "free" state, molecular hydrogen is a popular substance and demand for it is growing steadily. Not only is it used in a variety of products, from pharmaceuticals and food to most finished petroleum products and petrochemicals, but there is growing evidence that hydrogen is regarded in many countries as the best candidate for the honour of being called *the* fuel of the 21st century. This is primarily because when burned as a fuel, hydrogen releases considerable amounts of thermal energy (approximately three times that produced by methane for a given weight of fuel) and is essentially non-polluting. The principal combustion product is water.

In Canada, hydrogen and Alberta have a strong connection. Alberta is already Canada's largest producer and consumer of hydrogen, and all indications point to steady growth in both of these areas over the foreseeable future.

Thus, Alberta has a large stake in anything that affects the current hydrogen-producing and hydrogen-using industries. That is the principal reason why a number of Alberta companies and the Alberta government created a hydrogen technology research program in 1988.

This booklet is about hydrogen and what is being done today to harness its power. It describes the objectives of the Alberta Hydrogen Technology Research Program, and provides the reader with answers to some common questions.

Some Chemical and Physical Properties of Hydrogen

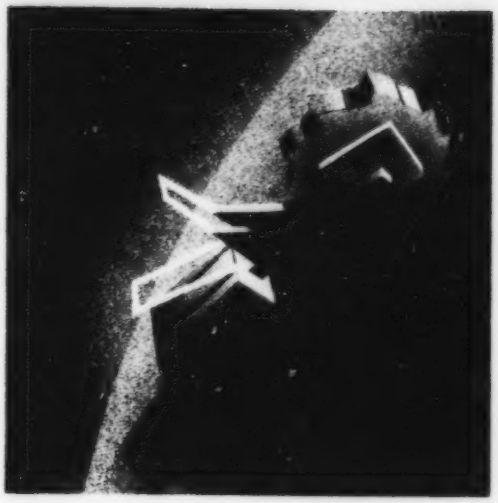
Hydrogen is a colourless, odourless, tasteless gas that is the lightest of all the elements. It occurs in an uncombined form in only the most minute fractions in the normal atmosphere; approximately one or two parts in 1 500 000 parts of air. The concentration may be much higher in gases issuing from volcanoes, petroleum-bearing areas and regions having large amounts of decaying organic matter.

Hydrogen is combined with carbon and/or oxygen in organic matter such as carbohydrates, hydrocarbons, fats and proteins. It is also found in rocks, soils, minerals and other ingredients of the earth's crust, but only in combination with oxygen. In addition, hydrogen is found combined with oxygen in water, the most abundant substance on earth. In fact, the name "hydrogen," given to the element in the 1700s, is derived from the Greek expression for "water producer."

While hydrogen-containing substances comprise less than one per cent of the earth's crust by weight, molecular hydrogen is more abundant in the upper atmosphere and its abundance increases with altitude. This is because hydrogen's low density enables it to rise to great heights. Much farther from the earth, the radiating envelope surrounding the sun's core is said to be 35 per cent hydrogen by weight, and the core itself is about 55 per cent hydrogen.

Under most conditions, molecular hydrogen is a gas. Very low temperatures are required to liquefy or solidify hydrogen. It liquefies at -252.78°C and freezes at -259.18°C. At the opposite end of the scale, temperatures in excess of 10 000°C are required to break the strong bonds holding a molecule of hydrogen together and completely dissociate it into two hydrogen atoms.

Similarly, hydrogen forms strong chemical bonds with oxygen to produce water. Thus, even though the abundance of water might suggest an easy way to make hydrogen, the energy required to break the hydrogen-oxygen bonds is somewhat greater than the energy released by hydrogen when it is burned. Therefore, liberating hydrogen from water and using it as a fuel results in a net energy loss. Consequently, although finding an economical way to make hydrogen has long been desirable, limited focus was placed on this research until warnings were sounded about the possible effect of carbon



dioxide on global warming. Now, researchers around the world are rushing to make up for lost time and are investigating a host of technical issues associated with producing and using hydrogen.

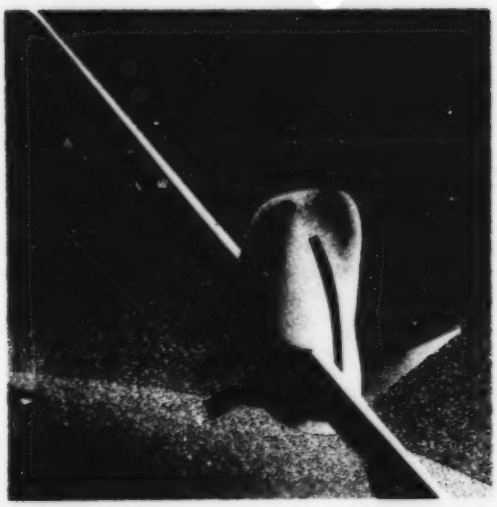
World-wide Developments

While environmental factors are currently the driving force behind this renewed interest in hydrogen, the substance has a number of other attractive features in its favour.

The principal advantage of hydrogen over other fossil fuel alternatives is its ability to be an energy "currency." This means it is a chemical energy carrier, rather than a primary source of energy. Like electricity, it has to be manufactured and, also like electricity, it is easily converted into other forms of energy. Because it can be stored and used as a fuel, it is very flexible in its uses. Perhaps most importantly, it is completely renewable. Just as the electrolysis of water produces hydrogen and oxygen, when the process is reversed and these two elements are combined, they produce water and heat or an electric current. This latter property has given rise to a separate, but related, field in which hydrogen-powered fuel cells are being developed. One of many such projects under way world-wide involves solid polymer fuel cells developed by a Vancouver firm and fuelled by hydrogen to produce power. These devices are being tested in several countries.

Because it is an energy currency, there are few situations in which hydrogen could not be used. In liquid form, it is already a reliable rocket fuel and, with proper mechanical handling systems, could be used in automobiles and airplanes. Thirty years ago, an American B-57 bomber flew a short distance using hydrogen in one engine after achieving flight altitude on conventional fuel. In April 1988, a Soviet jetliner accomplished a similar feat, but it took off, flew and landed using hydrogen in one engine.

In the U.S., some test automobiles have been fuelled by hydrogen for at least a decade, and the French auto firm, Peugeot, tested a hydrogen-fuelled car in the U.S. in 1981. Recently, German car makers BMW and Daimler-Benz announced they had initiated hydrogen fuel projects, and the Ontario government is currently investigating a system for powering electric cars involving hydrogen. These are only a few examples of work under way for hydrogen-fuelled vehicles.



The Role of Hydrogen in Canada

Perhaps the best report describing the hydrogen situation in Canada was produced in 1987. Called Hydrogen - National Mission for Canada, the report was produced for the federal government by the Advisory Group on Hydrogen Opportunities. The purpose of the Advisory Group's report was to spur Canadians into acting on the unique opportunities available to them to lead the world toward the Hydrogen Age.

Thus far, the national mission urged in the report has not emerged, but four provinces – British Columbia, Alberta, Ontario and Quebec – have stepped up activity in their individual hydrogen programs. Much of the emphasis of these programs is on finding economical ways to make hydrogen.

The most common method for producing hydrogen is through the catalytic action of steam on hydrocarbons, of which the steam-methane reforming process used in Alberta is the most common example. The general reactions are as follows:

$$C_nH_{2n+2} + nH_2O \leftrightharpoons nCO + (2n+1)H_2$$

and

$$C_nH_{2n+2} + 2nH_2O \leftrightharpoons nCO_2 + (3n+1)H_2$$

Up to 95 per cent of the CO is converted by further reaction with steam to hydrogen and carbon dioxide.

$$CO + H_2O \leftrightharpoons CO_2 + H_2$$

While the steam-methane reforming process is the least expensive commercial-scale method for producing hydrogen in Canada, the carbon dioxide it produces is currently vented to the atmosphere. This has now become a concern in the current debate about the causes of global warming.

Since the steam-methane reforming process currently produces most of Canada's hydrogen, an increasing demand for hydrogen also means an increasing demand for the natural gas from which it is produced. This need should benefit Alberta's gas industry.

In addition, coal gasification, a technology being developed in several countries including Canada, could become a source of hydrogen in Alberta during the coming decade. As with other hydrocarbons, the carbon in coal reacts with water to produce hydrogen and carbon monoxide:

$$C + H_2O \leftrightharpoons CO + H_2$$

In the future, electrolysis of water employing Canada's widely used hydroelectric capabilities should become a major source of hydrogen. Currently, a consortium of Quebec and European companies and the Quebec government is proposing to produce hydrogen by electrolysis and ship either it or a hydrogen-containing liquid product to Europe. The advantage of electrolysis over steam-methane reforming is that it uses a renewable source of energy, does not face any major engineering obstacles, and does not produce carbon dioxide. The costs, however, are approximately two to three times those of hydrogen produced by steam-methane reforming.

In Canada, ammonia production for the fertilizer industry accounts for approximately half of all hydrogen consumption. The remainder is divided among the petroleum and petrochemicals industries which use more than 30 per cent, the manufacturing of synthetic crude oil which consumes 10 per cent, and miscellaneous uses, such as food products, which account for the remaining 10 per cent. The comparable figures for Alberta are shown in the accompanying table.

Hydrogen Consumption in Alberta (tonnes/year)

Process	Consumption	%
Chemical		
Ammonia	523 000	41.1
Methanol	220 900	17.4
Oil Sands	201 600	15.8
Refining	75 700	5.9
Other Chemicals	7 600	0.6
Miscellaneous	1 400	0.1
Fuel		
Ammonia	9 400	0.7
Methanol	126 200	9.9
Oil Sands	24 600	1.9
Refining	28 900	2.3
Other Chemicals	37 400	3.0
Miscellaneous	200	-
Venting, Incineration	**16 100**	**1.3**
Total	**1 273 000**	**100**

(Source: Alberta Hydrogen Technology Inventory, RTM Engineering Ltd., 1988.)

Therefore, most of Canada's hydrogen consumption is by industries that dominate Alberta's economy, and most of the projected growth in hydrogen use is expected to be in these same industries.

An inventory of hydrogen production and use in Alberta was carried out in 1987/88. In addition to defining the extent to which hydrogen is produced and used in Alberta's petroleum and petrochemical industry, the study also found a growing use in applications such as food processing, steel production, metallurgy and the manufacture of pharmaceuticals.

It was found that Alberta industries produce 55 per cent and consume 63 per cent of all the hydrogen in Canada. Approximately 62 million cubic metres of hydrogen are produced in Alberta every day, having an annual value of $500 to $600 million.

While the greatest production and consumption are by ammonia and methanol producers, significant quantities of hydrogen are used in conventional oil refining. In a process called hydrotreating, hydrogen is added to improve the quality of refined products and reduce the emission of pollutants such as sulphur dioxide and phenols. When heavy oil is used as the feedstock in refineries, the hydrocracking process must be used. This requires substantial amounts of hydrogen. Also, hydrogen is essential for the production of synthetic crude oil from oil sand and heavy oil.

It is generally agreed that the greatest increase in production and use of hydrogen in the future will involve Alberta's hydrocarbon resources. In the near term, this growth will be associated with bitumen and heavy oil upgrading, but later it could include the production of transportation fuels from coal.

It has been estimated that the amount of hydrogen used to process a barrel of synthetic crude oil will double in 20 years from the current value. When combined with an anticipated increase in the demand for synthetic crude oil, this should cause hydrogen use in synthetic crude oil production to rise to as much as ten times the current usage by the end of this decade.

Coal liquefaction processes would require even larger amounts of hydrogen; some estimates suggest three or four times the amount used for synthetic crude production from oil sand.

Alberta Hydrogen Technology Research Program

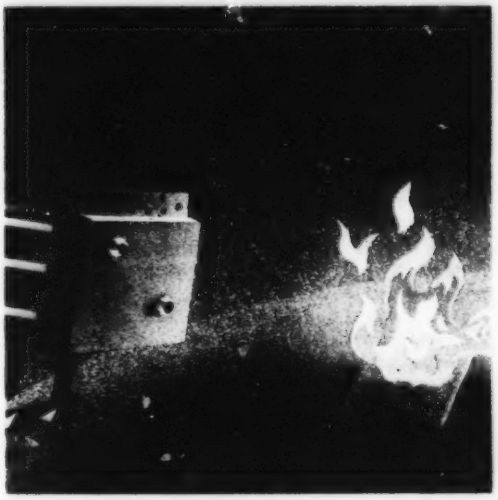
Because most of the expected growth in hydrogen use should arise from upgrading heavy oil and bitumen, and because the costs of hydrogen production currently represent a significant portion of overall upgrading costs, a joint industry/ government hydrogen technology research and development program was initiated in 1988/89.

The principal objectives of this program are to:

- protect and expand Alberta's petroleum industry by meeting the present and future market demands for higher hydrogen-to-carbon ratios in fuel products;
- develop technology for bulk merchant hydrogen sales; and
- develop marketable hydrogen technology based on fossil resources.

The program is being funded on a cost-shared basis by government and industry. Initially, government contributions were provided through the Alberta/ Canada Energy Resources Research Fund, which was supported jointly by the federal and Alberta governments. Currently, the program comprises the following components, each of which is considered to represent an aspect of hydrogen technology that will require commercial-scale development within 10 years. The components are:

- advanced or alternative hydrogen production technologies;
- production technologies that work synergistically with those being developed in a separate coal research program;
- hydrogen separation technologies;
- large-volume hydrogen storage;
- transportation/distribution of hydrogen;
- optimum end-uses of hydrogen; and
- materials and safety technology.



Hydrogen Production

Water (H_2O), methane (CH_4) and hydrogen sulphide (H_2S) are considered to be the three primary sources for hydrogen production in the immediate future in Alberta. These three feedstocks represent the richest, cheapest and most readily available hydrogen-containing sources. In particular, any process capable of economically splitting H_2S should produce only hydrogen and elemental sulphur, without the carbon dioxide by-product that results from steam-methane reforming.

In evaluating alternative hydrogen production technologies, they must be judged to be new or improved relative to steam-methane reforming. This requires evaluation of several factors, including process chemistry, energy input, process engineering, product separation and purification, and by-product uses.

Thus far, eight research projects have been initiated in Alberta to investigate various optional methods for producing hydrogen. They include thermal, catalytic or electrolytic decomposition of hydrogen sulphide.

Hydrogen Separation

Separation of produced hydrogen from unreacted feedstock or reaction by-products is one aspect of the Alberta Hydrogen Technology Research Program that deserves special attention. The choice of an appropriate separation technology could make the difference between a successful or unsuccessful hydrogen production method.

Although several straightforward hydrogen separation methods exist, combining these technologies with thermally or chemically energized hydrogen production processes is often inefficient or inappropriate. This result is frequently caused by large changes in the process temperature and pressure, or the use of separation processes that work only at low temperature. Some existing hydrogen-producing processes might become economically attractive if they could be combined with suitable separation methods.

For these reasons, two hydrogen separation research projects have been initiated thus far.

Infrastructure and Storage/ Transportation

The net hydrogen surplus currently existing at some Alberta facilities or locations may become larger as new or improved hydrogen production technologies are introduced. Fortunately, this surplus is expected to be offset by expansion of bitumen upgrading, increased synthetic fuel production and growth in the production of some specialty chemicals. All of these will consume hydrogen.

Thus, there is a need to move hydrogen from locations where it is produced in excess of on-site demand to those places where it is not produced but is needed. This requires methods for integrating producers and consumers.

Before an integrated producer/consumer network can be established, however, numerous technical issues must be addressed. One of the first requirements is for a strategy to link producers with consumers, including a staged development scheme.

Of equal importance is the investigation of several storage and transportation technologies. These will depend on the physical state of hydrogen when it is stored or transported, and must recognize that hydrogen can be handled as a gas, a liquid or metallic alloys called hydrides.

Transportation of hydrogen could involve combinations of truck, rail and pipeline systems. Like storage, this would require investigation of certain safety aspects and the physical effects of hydrogen on the storage or transportation medium.

Since 1989/90, three studies related to these issues have been initiated.

Hydrogen Use

The Alberta Hydrogen Technology Research Program places equal emphasis on improving the efficiency of current hydrogen-consuming processes and finding new uses for hydrogen in Alberta.

Two research projects related to this aspect of the program were initiated during 1990/91.

Future

Alberta has chosen to move into the hydrogen field by engaging in research having practical applications to today's problems, while fully recognizing that the technologies being developed will be important stepping-stones toward a future Hydrogen Age. This approach is consistent with the objectives of the National Mission as espoused in 1987 by the Advisory Group on Hydrogen Opportunities.

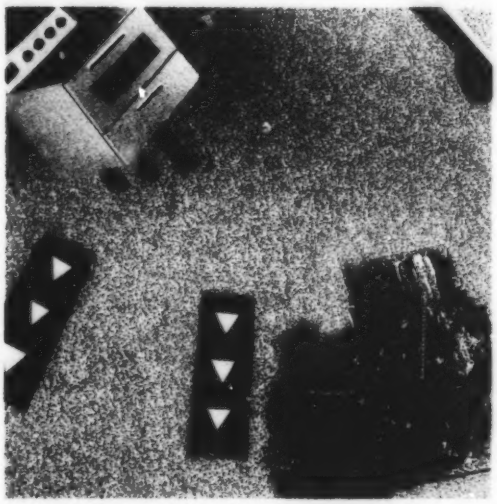
The Advisory Group believes that Canada should strive to accomplish the following:

- develop and own the best technologies for the economic production of hydrogen from either fossil or sustainable sources, and for hydrogen purification, distribution and storage;
- develop and own the world's best technologies for using hydrogen in the production of liquid fuels and other chemical products from fossil and biomass sources;
- develop and use the best technologies and most effective industrial interfacing to integrate energy sources whenever appropriate; and
- develop and own the best technologies, systems and products for using high purity hydrogen in vehicles.

Clearly, most of these objectives have a direct bearing on Alberta's energy industry.

In the Advisory Group report, the authors believed that the transition to hydrogen would be inevitable for the following reasons:

- the world is moving from exhaustible energy sources to sustainable sources;
- to be successful replacements for exhaustible energy sources, sustainable energy sources must be able to be used for the manufacture of chemical fuels and feedstocks;
- the only way sustainable energy sources can make chemical fuels and feedstocks world-wide and in large quantities is by producing hydrogen from water; and
- if the Greenhouse Effect is to be stalled, the only realistic approach is to use sustainable energy sources to produce the two renewable energy currencies, electricity and hydrogen, neither of which results in the production of carbon dioxide.



Projects Supported by the Hydrogen Technology Research Program to March 31, 1991.

Project	Researcher
Hydrogen Production	
Examination of the Partial Oxidation of Methane for the Production of Hydrogen and/or Synthesis Gas	G.A. Karim, University of Calgary, Calgary
A Claus Plant Modification for Hydrogen Production	Alberta Sulphur Research Ltd., Calgary
Conversion of Hydrogen Sulphide to Hydrogen and Organosulphur Compounds by Metal Catalysts	Alberta Sulphur Research Ltd., Calgary
Production of Hydrogen and Sulphur from Hydrogen Sulphide	L.G. Hepler, University of Alberta and J. Donini, CANMET, Edmonton and Devon
High-Temperature Electrolysis of Aqueous Hydrogen Sulphide for the Production of Hydrogen and Molten Sulphur	Alberta Research Council, Edmonton
Chemically Modified Electrodes for Hydrogen Sulphide Electrolysis	Alberta Research Council, Edmonton
The Carbon Monoxide Catalysed Conversion of Hydrogen Sulphide to Hydrogen and Sulphur	O.P. Strausz, University of Alberta, Edmonton
Cold Plasma Decomposition of Hydrogen Sulphide	Shell Canada Limited and Atomic Energy of Canada Limited, Calgary and Chalk River
Hydrogen Separation	
Hydrogen Separation and Purification	Alberta Research Council, Edmonton
High-Temperature Separation of Hydrogen Using Novel Ceramic Membranes	Alberta Research Council, Edmonton

Infrastructure and Storage/Transportation

Hydrogen Producer/ Consumer Network	Alberta Research Council, Devon
Salt Cavern Storage of Hydrogen	RTM Engineering Ltd., Calgary
Hydrogen Transportation Using Present Pipeline Networks	Hydrogen Industry Council, Calgary

Hydrogen Use

Optimization of Hydrogen Utilization in Heavy Hydrocarbon Processing	Alberta Chamber of Resources, Edmonton
Refinery By-product Hydrogen Use for Electricity Generation in Fuel Cells	TransAlta Utilities Corporation, Calgary

Other

Hydrogen Technology Program Planning and Implementation Assistance	Harold V. Page, Edmonton
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